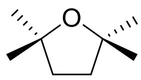
Sustainable Solvent Selection: Tools and Techniques for Bio-Based Solvent Substitution as Demonstrated by project ReSolve

Thomas J Farmer, F Byrne, J H Clark, AJ Hunt, J Sherwood

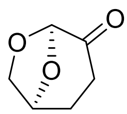
Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, UK, YO10 5DD, thomas.farmer@york.ac.uk

Sustainable Solvent Selection is a hot area of research, and it is desperately needed throughout the chemical industry as more a more traditional solvents come under ever increasing legislative strain. Our new H2020/BBI project **ReSolve** (2017-2020, grant agreement *745450*) sets out to replace two hazardous but widely used solvents – toluene and NMP (N-methyl-2-pyrrolidone) – with safer alternatives derived from non-food carbohydrates.[1] These new solvents will omit parts of the molecular structure that cause toxicity. The new, safer solvents will have a wide range of applications; project ReSolve will also demonstrate their sustainability, low health impact and high application performance. This talk will look in greater detail at two leading candidates currently under further investigation and scale-up.



TMO

1) An inherently non-peroxide forming ether solvent, 2,2,5,5-tetramethyloxolane (TMO), has been synthesized from readily available and potentially renewable feedstocks (acetone and acetylene), and its solvation properties determined.[2,3] Unlike traditional ethers, its lack of a proton at the α-position to the oxygen of the ether eliminates the potential to form hazardous peroxides whilst also making it suitable as solvent to replace toluene in radically-initiated polymerisations. TMO exhibits similar solvent properties to common hydrocarbon solvents (low dipolarity, low hydrogen-bonding ability), this demonstrated by its performance in a model amidation reaction. Furthermore, TMOs boiling point (112 °C), melting point (<-90 °C), density (0.802 g ml^{-1}), auto-ignition temperature (417 °C) and lower explosion limit (0.9%) are remarkably comparable to those of toluene.



Cyrene™

2) Cyrene (dihydrolevoglucoseneone) is a bio-based molecule, derived in two simple steps from cellulose, which demonstrates significant promise as a dipolar aprotic solvent. The dipolarity of Cyrene is similar to NMP, DMF and sulpholane and as such Cyrene demonstrates similar performance to NMP several applications including: fluorination and Menschutkin reactions,[4] Suzuki–Miyaura Cross-Coupling,[5] the synthesis of ureas,[6] and preparation of graphene via delamination of graphite.[7]

The talk with finish with a description of how our solvent selection techniques developed for the above to candidates are being further extended to seek other alternatives for the future.

[1] http://resolve-bbi.eu/
[2] F. Byrne, A. J. Hunt, T. J. Farmer, B. Forier and G. Bossaert, NL Pat, *P32826NL00/MKO* and *P32827NL00/WZO*, **2016**
[3] F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T.J. Farmer, J.H. Clark, A.J. Hunt, *Green Chem.*, **2017**,19, 3671-3678
[4] J. Sherwood, J.H.Clark, T.J. Farmer *et al.*, *Chem. Comm.*, **2014**, 50, 9650-9652
[5] K.L. Wilson, J. Murray, C. Jamieson, A.J.B. Watson, *Synlett*, **2017**, 28, A–E
[6] L. Mistry, K. Mapesa, T.W. Bousfield, J.E. Camp, *Green Chem.*, **2017**, 19, 2123–2128
[7] H.J. Salavagione, J. Sherwood, M. De bruyn, V.L. Budarin, G.J. Ellis, J.H. Clark, P.S. Shuttleworth, *Green Chem.*, **2017**,19, 2550-2560